Submitted to *J. Am. Chem. Sot.*

Experimental Demonstration of the Dependence of the First Hyperpolarizability of Donor-Acceptor Substituted Polyenes on the Ground-State Polarization and Bond Length Alternation

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ABSTRACT.

The dependence of the product of the first hyperpolarizability, β, and the ground-state dipole moment, μ, for a series of donor-acceptor polyenes with a large range of ground-state polarization, was measured in a variety of solvents by electric field induced second harmonic generation. The observed behavior of $\mu\cdot\beta$ as a function of ground-state polarization agrees well with theoretical predictions, In particular, as a function of increasing polarization, $\mu\cdot\beta$ was found to first increase, peak in a positive sense, decrease, pass through zero, become large and negative and eventually peak in a negative sense.

It has been suggested that optimizing the first hyperpolarizability, β, of donor-acceptor compounds requires a specific donor/acceptor strength for a given conjugated bridge.[1-3] For donor-acceptor polyenes, β can be maximized when an optimal degree of mixing between neutral and charge-separated canonical resonance forms exists.[2,4] This degree of mixing is related to the donor/acceptor strength and a molecular parameter, bond length alternation (BLA) defined as the difference between the average carbon-carbon single and double bond lengths in the polymethine backbone. The degree of BLA arises from the linear combination, or mixing, of the two-limiting charge-transfer resonance forms of the molecule (Figure 1).[4] For unsubstituted polyenes, or chromophores with weak donors/acceptors, the neutral canonical form is the dominant contributor to the ground state, resulting in large positive BLA. As the donor/acceptor strength increases, the charge-separated resonance structure contributes more to the ground state resulting in smaller BLA until both resonance forms contribute equally and the ground-state structure possesses essentially zero BLA analogous to a symmetrical cyanine.[5] Increasing the ground-state polarization further results in the charge-separated canonical form dominating the ground-state structure, leading to negative BLA.

The relationship between β and BLA can be understood within the context of a two-state model[6] in which the dominant component of the β tensor is given as:

$$\beta \propto (\mu_{ee} - \mu_{gg}) \frac{\mu_{ge}^2}{E_{ge}^2} \qquad (1)$$

where g (e) is the index of the ground (charge-transfer excited) state, μ and E are the dipole matrix element and transition energy between two subscripted states, respectively. It has been predicted[1,7] that as a function of increasing polarization (decreasing BLA), starting from the polyene limit (maximum positive BLA): (i) $\mu_{ee} - \mu_{gg}$, starts positive, increases and reaches a positive peak (region A, Figure 2); (ii) decreases, (region B); (iii) continues to decrease, passing through zero at the cyanine-limit, becomes negative (region C); (iv) becomes increasingly negative (region D) and (v) exhibits a negative peak and decreases in magnitude (region E), It is also predicted that μ_{ge}^2 and $1/E_{ge}^2$ peak at the cyanine-limit (Figure

2) and thus β, which is a product of these three terms, exhibits positive and negative peaks closer to the cyanine-limit than where ($\mu_{ee} - \mu_{gg}$) peaks. In this paper, molecular second-order nonlinear optical properties ofa series of donor-acceptor polyenes have been evaluated by electric field induced second harmonic generation (EFISH) to test the structure-property relationships proposed in Figure 2.

Molecules 1-6 (Figure 1), synthesized using literature procedures,[4,8-10] were examined since strong evidence exists that they cover approximate] y the BLA range A-E (Figure 2). For example, BLA values for 1 and 2, determined by X-ray crystallography, are 0.05 Å and <0,02 Å respectively, suggesting that 1 lies in region A and 2 in region B.[11] X-ray crystallographic studies[12] on 4, possessing a stronger acceptor than 1 or 2, reveal a BLA of -0.014 Å, suggesting that 4 lies in region C, Additionally, 3 and 4 exhibit positive solvatochromism in nonpolar solvents and negative solvatochromism in polar solvents (Table I), indicative of BLA changing sign as a function of solvent polarity. 10 These data suggest that 3 and 4 fall in region C. Compounds 5 and 6 are negatively solvatochromic in all solvents used. Furthermore, the large $^1H - ^1H$ coupling constant (14.91 and 15,21 Hz for 5 and 6, respectively, in $CDCl_3$) across the central carbon-carbon bond is consistent with a trans double bond as depicted in the zwitterionic form of 5 and 6 (Figure 1 right). These data imply that 5 falls in region D and that 6 falls in D in moderate polarity solvents and possibly region E in highly polar solvents. For a given molecule, BLA can be fine-tuned by varying solvent polarity since mixing of the neutral and charge-separated canonical forms is sensitive to this perturbation.[10,11,14,15]

Non-resonant EFISH measurements of $\mu \cdot \beta$ were performed, at 1907 nm, on 1-6 in solvents of varying polarity using an apparatus and methodology described elsewhere.[16] The $\mu \cdot \beta$ product and absorption maxima as a function of the normalized solvent polarity parameter $E_T(30)$[13] are presented in Table I. The $\mu \cdot \beta$ product of 1 increases with solvent polarity, consistent with the hyperpolarizability trend expected given the large BLA from previous structure determinations.[11] The strength of the donor/acceptor pair is insufficient therefore to obtain the particular ground-state polarization or BLA required to optimize β in a positive sense. When the stronger dicyano moiety (2) replaces the aldehyde

acceptor, the contribution of the charge-separated canonical form to the ground state increases, BLA decreases and $\mu\cdot\beta$ exhibits a positive peak (region B of Figure 2). A positive peak in $\mu\cdot\beta$ has been reported previously for dimethylindoaniline.[1] Increasing the acceptor strength further by utilizing the diethylbarbituric (3) and diethylthiobarbituric acid (4) moieties, results in decreasing hyperpolarizabilities with increasing solvent polarity. In fact, for 3 in the most polar solvent and 4 in nonpolar solvents $\mu\cdot\beta$ ***changes sign,*** consistent with the structural assignment above of 3 and 4 being in region C. This sign change occurs as a result of solvent stabilization of the charge-separated canonical form tuning BLA through the cyanine-limit.10 This is the first observation of a sign change in $\mu\cdot\beta$ as a function of changing an external property, without tuning through a resonance. The values of λ_{max} for 4 are maximized when $\mu\cdot\beta$ is close to zero, consistent with the relationship depicted in Figure 2. As the donor/acceptor strength is further increased (5 and 6), a negative peak in $\mu\cdot\beta$, with increasing solvent polarity, is observed consistent with the predicted behavior for region D. While there have been reports of negative $\mu\cdot\beta$ values 17 and solvent-dependent negative $\mu\cdot\beta$ values, [1]5 this is the first report of the ***optimization*** of $\mu\cdot\beta$ in a negative sense.

In summary, donor-acceptor polyenes of comparable conjugation length have been synthesized and their solvent-dependent, non-resonant hyperpolarizabilities probed by EFISH. Optimization in both a positive and negative sense as well as a sign change of $\mu\cdot\beta$ was observed. These observations were explained by molecular structure changes resulting from the variation of mixing of neutral and charge separated resonance forms upon changing the donor/acceptor strengths and solvent polarity. The trend of these geometry-dependent hyperpolarizabilities is fully consistent with the trend theoretically predicted.

Acknowledgment.

The research described in this paper was performed n part by the Jet Propulsion Laboratory, California Institute of Technology, as part of its Center for Space Microelectronics Technology and was supported by the Advanced Research Projects Agency (administered by the Air Force Office of Scientific Research) and the Ballistic Missiles Defense Initiative Organization, Innovative Science and Technology

Office, through a contract with the National Aeronautics and Space Administration (NASA). Support at the Beckman Institute from the National Science Foundation (grant # CHE-9106689) and the North Atlantic Treaty Organisation is gratefully acknowledged, G. B. thanks the National Research Council and NASA for a Resident Research Associateship at JPL. The work by F. M. is carried out within the framework of the Belgium Prime Minister Office of Science Policy "Pole d'Attraction Interuniversitaire en Chimie Supramoleculaire et Catalyse". The authors would like to thank Dr. Brian M. Pierce for helpful discussions, Howard D. Jones for expert technical assistance, Matthew J. Perry for the synthesis of **5** and Ging Lee for providing the coupling constant data.

Supplementary Material:

^{1}H nuclear magnetic resonance spectroscopic and elemental analytical data for 3-6 and X-ray crystallographic data for 4 (40 pages). Ordering information is given on any current masthead page.

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Figure captions

Figure 1. Canonical charge-transfer resonance structures for the donor-acceptor polyenes investigated. Electron donor/acceptor strength in the neutral form increases from **1-6**. Et= C2H5 and Bu ≡ *n*-C_4H_9.

Figure 2. The dependence of the ground-state structure on μ_{ge}^2 (- -- -), $1/E_{ge}^2$ (····), $\mu_{ee} - \mu_{gg}$ (– – – –) and β (—) in arbitrary units for $(CH_3)_2N\text{-}(CH{=}CH)_4\text{-}CHO$. Ground-state polarization increases from regions A-E. The point at which both $(\mu_{ee} - \mu_{gg})$ and β are zero corresponds to the "cyanine-limit" of zero BLA (center of region **C**).

Table I. Solvent-dependent $\mu\cdot\beta$ (units of 10^{-48} esu) for molecules 1-6 (given ***in*** boldface). The estimated precision in the $\mu\cdot\beta$ values is ±10%. The polarity of the solvents increase (the contribution of the charge-separated resonance structure to the ground-state geometry increases) from left to right. The normalized $E_T(30)$[13] values of the solvents are presented within parenthesis. The wavelength of maximum absorption (λmax, units of nm) of the chromophores are given below the $\mu\cdot\beta$ values. Insolubility precluded the determination of $\mu\cdot\beta$ for 5 and 6 in certain solvents.

	Solvent						
Molecule	CCl_4 (0.0525)	C_6H_6 (0.1111)	$CHCl_3$ (0.2593)	CH_2Cl_2 (0.3086)	CH_3CN (0.4560)	CH_3NO_2 (0.4815)	Region
1 $\mu\cdot\beta$	299	272	322	343	348	430	A
λmax	396	404	420	420	418	426	
2 $\mu\cdot\beta$	332	360	400	***340***	231	195	B
λmax	446	472	478	***480***	476	480	
3 $\mu\cdot\beta$	401	205	200	***141***	109	-65	**C**
λmax	498	504	510	***508***	502	506	
4 $\mu\cdot\beta$	2’76	264	-22	***-60***	-240	-316	**C**
λmax	526	532	536	***534***	524	526	
5 $\mu\cdot\beta$	.	-180	-374	***-414***	.	-350	D
λmax	528	520	510	***506***	488	490	
6 $\mu\cdot\beta$	.	.	-600	***-770***	-550	-363	**D/E**
λmax	548	538	526	***520***	496	496	

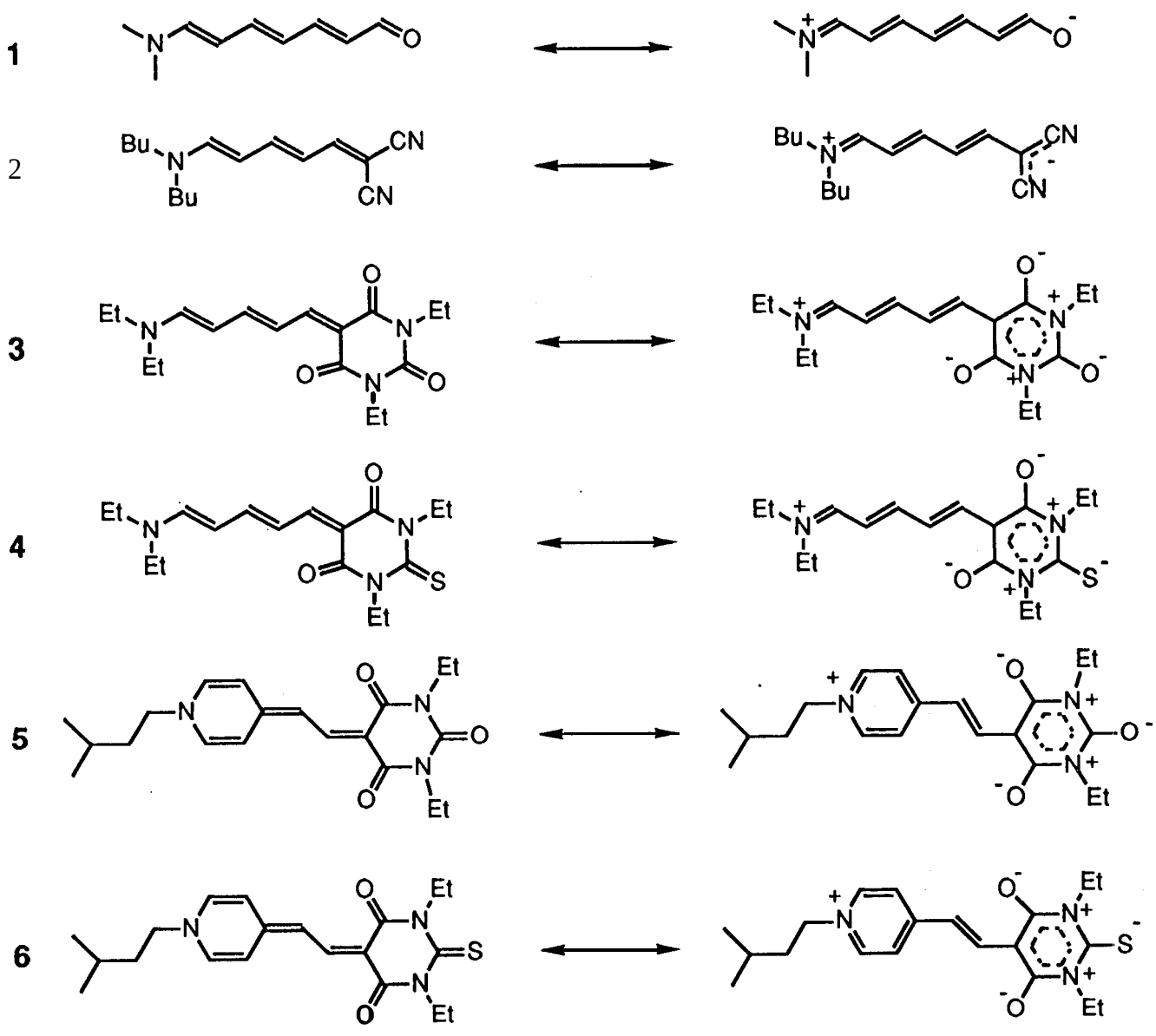

Figure 1: Bourhill et al.

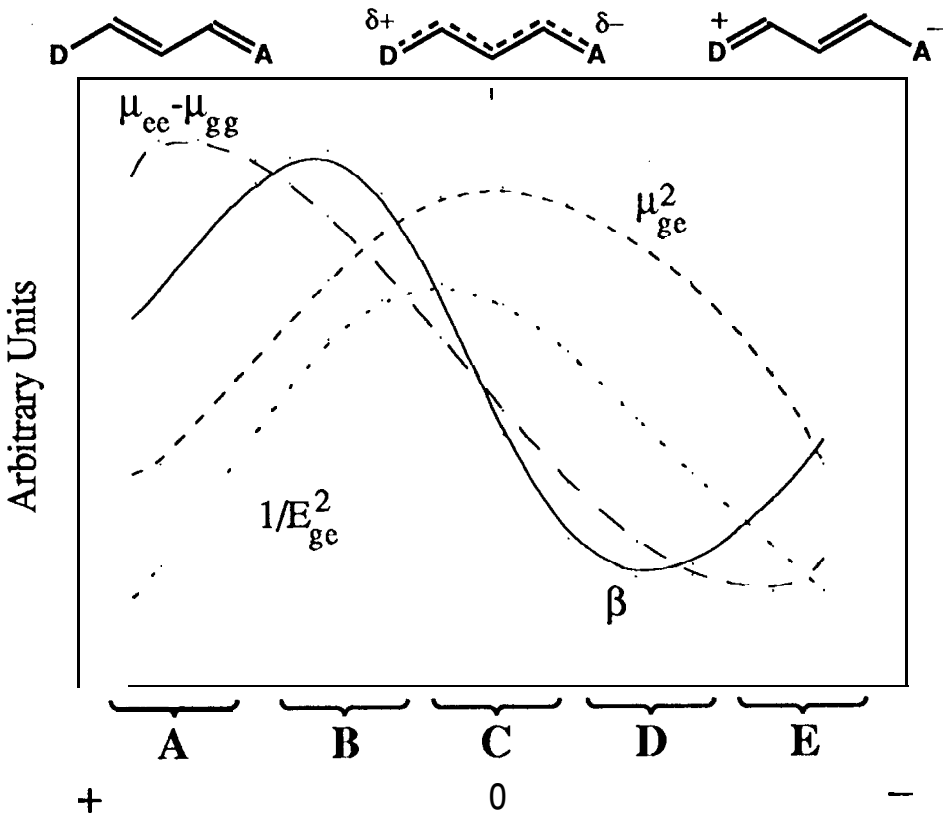

Figure 2: Bourhill et al.